$A_\pi{}^I$ and $A_\pi{}^{II}$ are zero because $f_{p\pi}=f_{p\pi'}$. It should be noted that in Eqs. (34), (35), and (36) we have assumed that the degree of unpairing in the p orbitals is uniform throughout each orbital. This is not, in fact, the case since the cross term shown in Eq. (30) is a function of the distance between the Mn ion and the point in the p orbital at which the unpairing is to be calculated. We are therefore neglecting entirely the effect of the cross term in assuming the unpairing to be uniform and equal to the square of the overlap integral. This procedure probably introduces little error in the calculation of $H_{i.c}$ and dH_∞/dP because the inner dipole contribution to these quantities is in itself quite small. Using[36] $\langle 1/r^3 \rangle = 44.4 \times 10^{24}/\mathrm{cm}^3$, we find the value of $(H_\infty)_{i.d.}$ listed in Table IV.

The pressure dependence of $(H_\infty)_{i.d.}$ is given by

$$\left(\frac{\partial H_\infty}{\partial P}\right)_{i.d.} = \frac{2}{5}\left\langle\frac{1}{r^3}\right\rangle\frac{g\beta}{2}\left(2\lambda\frac{\partial(f_{p\sigma}{}^I - f_{p\pi'}{}^I)}{\partial r_I}\frac{\partial r_I}{\partial P}\right.$$
$$\left. +\frac{\partial(f_{p\sigma}{}^{II}-f_{p\pi'}{}^{II})}{\partial r_{II}}\frac{\partial r_{II}}{\partial P}+2(f_{p\sigma}{}^I-f_{p\pi'}{}^I)\frac{\partial\lambda}{\partial P}\right). \quad (37)$$

The magnitude of this term is listed in Table IV.

It is clear from the last two rows of Table IV that the theoretical calculations of H_∞ and dH_∞/dP are in excellent agreement with the experimental results.

It may be worthwhile to emphasize that the theory outlined above does not require the inclusion of any covalency, in that we do not include the unpairing effect of fluorine electrons "hopping" into d states on the manganese ion. Clearly our results indicate that this is well justified at least in connection with the s-state electrons. "Hopping" out of p orbitals may affect the f_p's somewhat, however, as has been noted above, the error thereby produced in the calculation of H_∞ and dH_∞/dP will be quite small due to the small contribution of the inner dipole field.

[36] R. G. Barnes and W. V. Smith, Phys. Rev. 93, 95 (1954).

IV. CONCLUSIONS

From our measurements of the pressure dependence of the zero field nuclear magnetic resonance frequency of the F^{19} nucleus in antiferromagnetic MnF₂, we have deduced the pressure dependence of the Néel temperature, and the pressure dependence of the hyperfine interaction between the fluorine nucleus and the manganese electrons. No theoretical explanation is offered for the pressure dependence of T_N.

The theories of Mukherji and Das, and Marshall and Stuart are used to explain the magnitude and pressure dependence of the hyperfine interaction. The theory uses the Hartree self-consistent field wave functions for free fluorine ions, with the Hartree solution for the Mn^{2+} ion slightly altered to bring it into agreement with neutron scattering form factor measurements. The electron unpairing responsible for the hyperfine interaction is calculated solely from the effects of exchange correlation which arise directly out of the Pauli Exclusion Principle. Agreement between theory and experiment is very good.

V. ACKNOWLEDGMENTS